

Reactivity Control of a Dinuclear Xenophilic Species, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$, via Spin Crossover across a Metal-metal Bond [$\text{Tp}^\#$: Hydrotris(4-bromo-3,5-dimethylpyrazolyl)borato]

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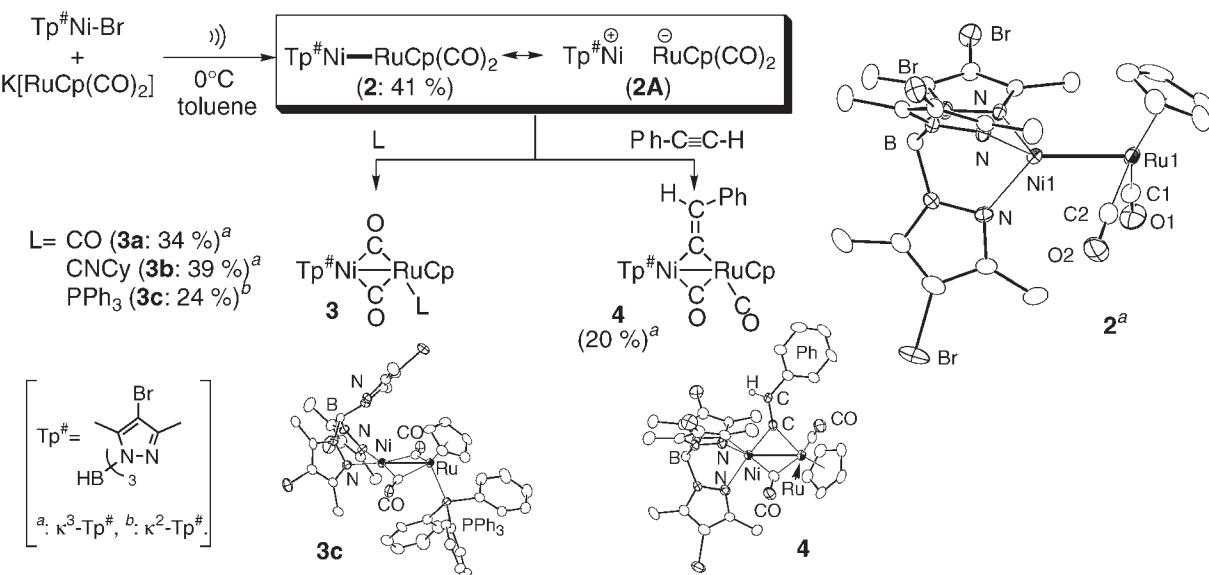
(Received August 13, 2002; CL-020690)

A high-spin, triplet xenophilic complex, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$, readily reacted with 2e-donors (L) via spin crossover at Ni associated with transposition of the resultant coordinatively unsaturated site from Ni to Ru to give diamagnetic adducts, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\mu-\text{CO})_2(\text{L})$.

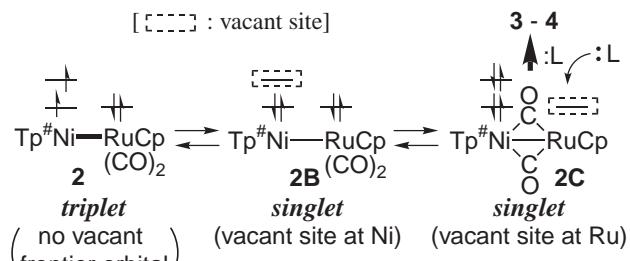
High spin organometallics are expected to display unique properties and reactivities distinct from those of closed-shell, diamagnetic organometallic species but their chemistry has not been thoroughly explored.¹ In particular, the relationship between the spin state and stability (reactivity) of electron-deficient, coordinatively unsaturated species is still in controversy. Xenophilic complexes are a polynuclear version of high spin species having a polar metal-metal bond between a coordinatively unsaturated Wernerian metal fragment and a coordinatively saturated organometallic fragment.² Previously we reported a rational synthetic method for a series of xenophilic complexes, $\text{Tp}^\# \text{M}-\text{Co}(\text{CO})_4$ **1**,³ containing the $\text{Tp}^\# \text{M}$ -type Wernerian metal fragment with $\text{Tp}^\#$ [hydrotris(pyrazolyl)-borato]⁴ featured as a tetrahedral enforcer. Because, however, complexes **1** were too unstable to be scrutinized, reactivity of $\text{Tp}^\# \text{M}-\text{M}'\text{L}_n$ -type complexes is yet to be characterized. Herein we wish to report (i) synthesis of $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$ **2**,⁵ the first example of a xenophilic complex containing a second row metal fragment, and (ii) a new type of reactivity of a dinuclear species emerging via spin crossover across a metal-metal bond.

The heterobimetallic xenophilic complex **2** was prepared by

sonication of a toluene suspension of $\text{Tp}^\# \text{Ni}-\text{Br}$ and $\text{K}[\text{RuCp}(\text{CO})_2]$ (Scheme 1).⁶ The dark brown complex **2** shows chemical properties⁷ similar to those of **1**, i.e. (i) coordinatively unsaturated species with 32 valence electrons (VEs) (short of 2 VEs from a saturated structure), (ii) paramagnetic, high-spin species with a triplet ground state (μ_{eff}), (iii) connection of the two metal centers only by the metal-metal bond (no μ -CO ligand), and (iv) the polarized metal-metal bond (**2A**) [shift of the $\nu(\text{CO})$ vibrations to lower energies]. These features are also supported by X-ray crystallography.⁸ The $\text{Tp}^\# \text{Ni}$ and $\text{RuCp}(\text{CO})_2$ moieties adopt a typical tetrahedral and three-legged piano-stool structure, respectively, and the distance of the unsupported Ni-Ru bond [2.512(1) Å] is slightly shorter than those in the adducts with additional bridging ligands [2.576(1) (**3b**), 2.560(1) (**3c**), 2.579(1) Å (**4**); see below]. The CO ligands are η^1 -bonded to the Ru center with no bridging interaction with the Ni center as is evident from the linear Ru-C-O linkage [C1-O1: 175.9(8)°; C2-O2: 176.5(8)°] and the Ni···CO separations [Ni1···C1: 2.866(9) Å; Ni1···C2: 2.761(8) Å]. Despite the coordinatively unsaturated 32 VE structure, complex **2** turns out to be thermally stable, although it is sensitive to the air and moisture. The thermal stability has been ascribed to lack of a vacant frontier orbital, i.e. all frontier orbitals are occupied by electron pairs or unpaired electrons to lead to the high spin, triplet electronic configuration (see structure **2** in Scheme 2). These features are in line with the formulation as a xenophilic complex, where the tetrahedral, high spin, coordinatively unsaturated Ni fragment is bonded to the coordinatively saturated Ru center.



Scheme 1.



Scheme 2.

Despite the lack of a vacant coordination site the xenophilic complex **2** readily reacted with donors under ambient conditions to afford the coordinatively saturated adducts **3** with 34 VEs (Scheme 1). Adduct formation was also observed upon treatment with phenyl acetylene, which produced the μ -vinylidene complex **4** showing the deshielded α -carbon signal (δ_C 251.7). The diamagnetic products **3** and **4** were characterized by spectroscopic methods⁷ and molecular structures of **3b,c**, and **4** were confirmed by X-ray crystallography.⁸ It is notable that (i) the xenophilic complex **2** without a vacant frontier orbital reacts with donors under mild conditions, (ii) diamagnetic products **3** and **4** are obtained from the paramagnetic species **2**, (iii) donors don't add to the electron-deficient Ni center in **2** but to the Ru center, and (iv) the two CO ligands in **2** are shifted from the terminal positions to the bridging positions. The first two points suggest occurrence of spin crossover.

The results obtained can be interpreted in terms of Scheme 2.^{9,10} Judging from the structures of the adducts **3-4**, the reactive form of **2** would be a singlet species with two bridging CO ligands having a vacant site at the Ru center (**2C**). Intermediate **2C** would be formed via terminal-bridging site exchange of the CO ligands of the singlet form **2B** with the vacant site at Ni, which results from spin crossover of the original triplet form **2**. Thus the triplet species **2** reacts with electron donors through spin crossover at Ni (**2B**) followed by transposition of the resultant vacant site across the metal-metal bond, which integrates the dinuclear structure. There has been much controversy about spin crossover of organometallic species. For example, Schrock^{1c} proposed the concept of "spin-blocking", which accounted for the slow reaction of a coordinatively unsaturated high spin species toward a 2e-donor, whereas Theopold^{1d} is opposed to claiming such a tendency as a general rule. While direct evidence for **2B,C** has not been obtained, the present system can be regarded as a dinuclear version of the spin crossover system with no substantial barrier between the two spin states, as judged by the reaction features.

In conclusion, the high spin, xenophilic complex **2** is formally described not only as a resonance hybrid with the zwitterionic structure **2A** but also as an equilibrated mixture with the singlet, coordinatively unsaturated form **2C** resulting from spin crossover across the metal-metal bond, and this type of behavior is a unique feature of xenophilic species.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (11228201) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References and Notes

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- 5 $Tp^{\#}$: hydrotris(4-bromo-3,5-dimethylpyrazolyl)borato.
- 6 Sonication of a toluene suspension (10 mL) of $Tp^{\#}$ -Ni-Br (300 mg, 0.446 mmol) and $K[RuCp(CO)_2]$ [prepared by reduction of $Ru_2Cp_2(CO)_4$ (149 mg, 0.335 mmol) with Na-K alloy in THF and dried in *vacuo*] gave brown precipitates, which were extracted with CH_2Cl_2 and crystallized from CH_2Cl_2 -hexane. **2**: dark brown crystals (148 mg, 0.181 mmol, 41% yield). The reaction without sonication afforded a mixture of products, because the reaction was so slow as to cause concomitant decomposition of **2**.
- 7 Selected spectroscopic data: **2**: IR (KBr) 2553 (ν_{BH}), 1953, 1891 cm^{-1} (ν_{CO}). $\mu_{eff} = 2.92 \mu_B$. **3a**: 2533 (ν_{BH}), 2013, 2003, 1858, 1846, 1815, 1801, 1801 cm^{-1} (ν_{CO}). δ_H (CD_2Cl_2) 5.61 (Cp), 2.35 (18H, s, Me). δ_C (CD_2Cl_2 , -90°C) 240.6, 199.8 (CO). **3b**: 2519 (ν_{BH}), 2173 (ν_{CN}), 1842, 1793 cm^{-1} (ν_{CO}). δ_H 5.40 (5H, s, Cp), 2.33 (18H, s, Me). δ_C 246.5 (CO), 143.0 (CN). **3c**: 2472 (ν_{BH}), 1962, 1821, 1772 cm^{-1} (ν_{CO}). δ_H 4.92 (Cp), 2.22 (9H, s, Me), 2.04 (9H, s, Me). δ_C 242.8 (d, $J_{CP} = 12.1 \text{ Hz}$, CO). δ_P 46.5. **3d**: 2536 (ν_{BH}), 2137 (ν_{CN}), 1994, 1832, 1788 cm^{-1} (ν_{CO}). δ_H 5.55 (Cp), 2.37 (6H, s, Me), 2.33 (3H, s, Me), 2.23 (6H, s, Me), 1.90 (3H, s, Me). δ_C 245.3 (CO), 156.9 (CN). **4**: 2524 (ν_{BH}), 2017, 1843 (ν_{CO}), 1588 cm^{-1} ($\nu_{C=C}$). δ_H 5.86 (Cp), 5.32 (1H, s, =CH), 2.46, 2.41, 2.36, 2.28, 1.94, 1.73 (3H x 6, s x 6, Me). δ_C 251.7 (C_{α}), 236.7, 201.2 (CO), 134.8 (=CH).
- 8 X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector at -60°C . Crystal data: **2**: $C_{22}H_{24}N_6O_2B-Br_3NiRu$, fw = 814.8, monoclinic, space group $P2_1/n$, $a = 12.3721(8) \text{ \AA}$, $b = 15.2504(4) \text{ \AA}$, $c = 15.955(1) \text{ \AA}$, $\beta = 95.1083(7)^{\circ}$, $V = 2998.5(3) \text{ \AA}^3$, $Z = 4$, $d_{calcd} = 1.81 \text{ g}\cdot\text{cm}^{-3}$, $R1 = 0.061$ (refined on F^2) for 5064 data ($F > 4\sigma(F)$), $wR2 = 0.204$ (all data). **3b** (hexane)_{0.5}: $C_{32}H_{42}N_7O_2BBr_3NiRu$, fw = 967.0, triclinic, space group $\bar{P}1$, $a = 12.5785(3) \text{ \AA}$, $b = 16.3823(5) \text{ \AA}$, $c = 11.6444(5) \text{ \AA}$, $\alpha = 107.073(1)^{\circ}$, $\beta = 109.643(2)^{\circ}$, $\gamma = 68.034(5)^{\circ}$, $V = 2056.7(1) \text{ \AA}^3$, $Z = 2$, $d_{calcd} = 1.56 \text{ g}\cdot\text{cm}^{-3}$, $R1 = 0.058$ for 6832 data ($F > 4\sigma(F)$), $wR2 = 0.188$ (all data). **3c**· CH_2Cl_2 : $C_{41}H_{41}N_6O_2BPBr_3NiRu$, fw = 1162.0, triclinic, space group $\bar{P}1$, $a = 12.628(1) \text{ \AA}$, $b = 15.784(3) \text{ \AA}$, $c = 12.553(1) \text{ \AA}$, $\alpha = 91.157(7)^{\circ}$, $\beta = 114.240(8)^{\circ}$, $\gamma = 83.816(6)^{\circ}$, $V = 2267.5(6) \text{ \AA}^3$, $Z = 2$, $d_{calcd} = 1.70 \text{ g}\cdot\text{cm}^{-3}$, $R1 = 0.075$ for 6008 data ($F > 4\sigma(F)$), $wR2 = 0.201$ (all data). **4**: $C_{36}H_{44}N_6O_2BBr_3NiRu$, fw = 1003.1, triclinic, space group $\bar{P}1$, $a = 12.044(2) \text{ \AA}$, $b = 16.873(3) \text{ \AA}$, $c = 11.170(2) \text{ \AA}$, $\alpha = 96.099(6)^{\circ}$, $\beta = 113.258(5)^{\circ}$, $\gamma = 104.55(1)^{\circ}$, $V = 1963.8(6) \text{ \AA}^3$, $Z = 2$, $d_{calcd} = 1.70 \text{ g}\cdot\text{cm}^{-3}$, $R1 = 0.068$ for 5316 data ($F > 4\sigma(F)$), $wR2 = 0.190$ (all data).
- 9 Complex **4** should be formed via coordination of $\text{Ph}-\text{C}\equiv\text{C}-\text{H}$ at Ru in **2C**, 1,2-H-shift giving a η^1 -vinylidene ligand and site exchange with the μ -CO ligand. M. I. Bruce, *Chem. Rev.*, **98**, 2797 (1998).
- 10 Analogous addition reactions were also observed for **1** ($M = \text{Ni}$, $Tp^R = Tp^{\#}$) and, therefore, these types of properties can be regarded as unique properties of xenophilic complexes containing a $Tp^R M$ fragment. K. Uehara, S. Hikichi, and M. Akita, unpublished results.